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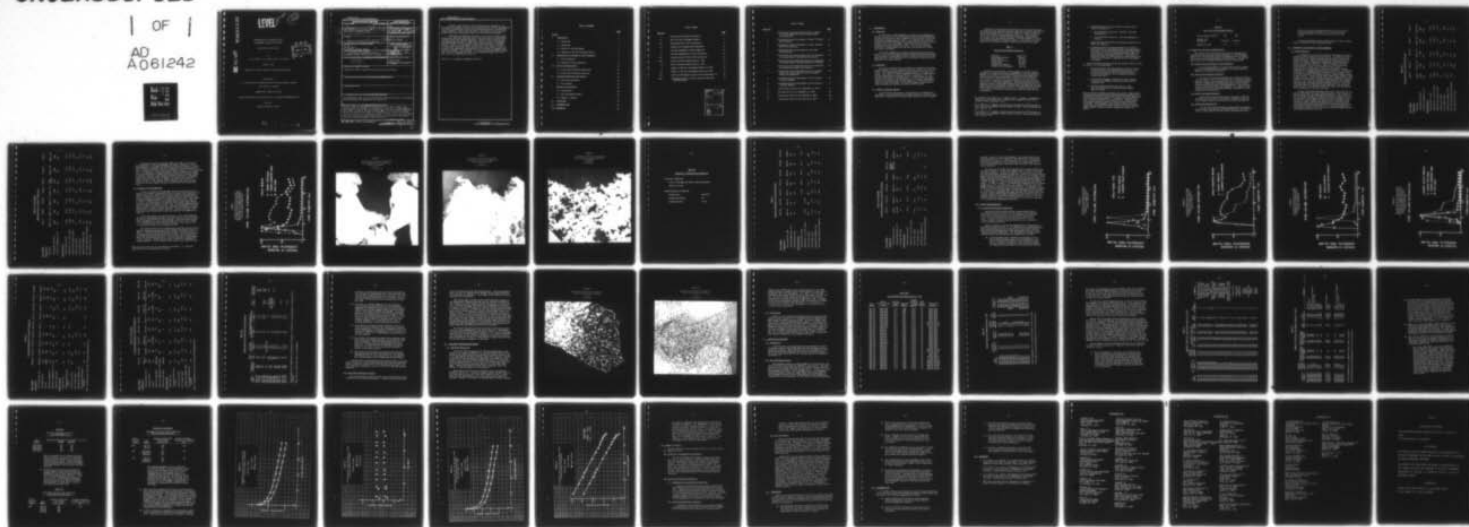
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OPTIMIZATION OF PT-DOPED KOCITE^R
ELECTRODES IN H₃PO₄ FUEL CELLS

Interim Technical Report

by

L. B. Welsh, R. W. Leyerle and D. M. Preston

August, 1978

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Prepared for

U. S. Army Mobility Equipment Research and Development Command

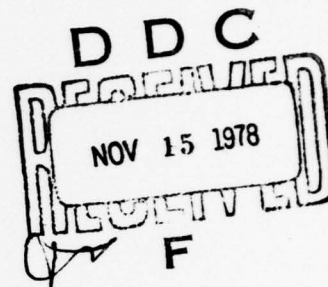
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Different types of Kocite electrocatalysts were produced by first leaching of the alumina substrate from a Kocite material and then impregnating the resulting pyropolymer structure with platinum using one of several different techniques. Kocite electrocatalysts fabricated by these techniques normally have a $650 \text{ m}^2/\text{g}$ surface area for a 15 wt-% platinum loading.

PTFE-bonded gas diffusion electrodes, with a porous graphite-paper backing were fabricated from these Kocite electrocatalysts by both machine-calendering and sheet molding techniques. Typical Kocite electrode platinum loadings were $0.6 \text{ mg}/\text{cm}^2$. Model fuel cell test results were normally obtained at 180°C with air cathodes and H_2 anodes operated at atmospheric pressure. Recent cell testing has stressed the use of Kocite electrodes as both anodes and cathodes while testing large enough numbers of cells to determine cell performance reproducibility with current cell assembly techniques and hardware. In one series of 15 test cells 80% performed at better than 550 mV at $200 \text{ mA}/\text{cm}^2$ and 180°C . The average performance was 575 mV with a best cell performance of 600 mV.

*"Kocite" is a registered trademark of UOP Inc.

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I. INTRODUCTION

1.1 Objectives

The objective of this program is to optimize the performance of low-cost air and fuel electrodes fabricated from platinum-impregnated UOP Kocite materials for use in phosphoric-acid-electrolyte fuel cells operating at temperatures near 180°C. To accomplish this objective, various Kocite electrocatalysts are produced and fabricated into state-of-the-art fuel cell electrodes. These electrodes are tested as cathodes and anodes in model fuel cells. The cell testing determines both the performance level and long term endurance attainable with Kocite electrodes.

This report summarizes the results obtained during the last six months. Both the Kocite electrocatalyst formulations prepared during this period and the performance levels attained with Kocite electrodes made from these electrocatalysts will be discussed, along with recommendations for future research.

1.2 Background

The current research effort continues the optimization of Kocite electrocatalysts for use in phosphoric-acid-electrolyte fuel cell electrodes. The program organization established earlier is being continued. This involves a joint program with UOP Inc. as prime contractor and Energy Research Corporation (ERC, a subsidiary of St. Joe Minerals Corporation) as subcontractor. A broad division of effort is made on the basis of the UOP capability to produce Pt-impregnated Kocite electrocatalysts and the ERC capability to fabricate and optimize electrode structures. Testing and diagnostic evaluations of these electrodes are carried out jointly by UOP and ERC.

1.3 Review of Previous Results

In this section the status of this program at the beginning of the present contract period will be briefly reviewed to provide a background for a discussion of the effort made during the last six months.

The nature of Kocite materials and many of the process conditions for preparing these materials have been described in earlier reports.^{1,2,3} During the previous contract periods a number of different Kocite materials were examined as electrocatalyst supports. This evaluation led to the choice of a Kocite material using Alcoa's Hydral 705 as the standard starting substrate material. Relevant properties of this type of Kocite material are given in Table I. The majority of Kocite materials used during the present contract period are of this type.

Table I

Typical Kocite Material Properties

Substrate	Hydral 705
Pyropolymer Precursor	Benzene
Carbon Content	~25 wt-%
Resistivity at 25°C	~0.1 Ω -cm
Surface Area	~80 m ² /g
Average Pore Diameter	~6 nm
Average Particle Diameter	~0.5 μ m

During the early portions of this program, all Kocite electrocatalysts were prepared by platinum impregnation of Kocite materials. However, as a result of the discovery that the alumina substrate is leached from small Kocite particles by phosphoric acid during fuel cell operation, it was believed that improved Kocite electrocatalysts could be obtained by leaching the alumina from the Kocite particles prior to platinum impregnation. The resulting Kocite electrocatalysts consist of very small platinum particles supported on a very high-surface-area pyropolymer structure, which replicates the starting alumina particle shape and pore structure. During the previous contract period electrocatalyst production was directed toward the following goals:

- ¹L. B. Welsh, R. W. Leyerle, G. L. Hervert and K. J. Youtsey, "Carbonaceous Catalysts for H₃PO₄ Fuel Cells", MERDC Contract DAAK02-75-C-0011, Final Technical Report, September, 1975.
- ²L. B. Welsh, R. W. Leyerle, "Optimization of Pt-Doped Kocite^R Electrodes in H₃PO₄ Fuel Cells", MERADCOM Contract DAAG53-76-C-0014, Interim Technical Report, January, 1977.
- ³L. B. Welsh, R. W. Leyerle, "Optimization of Pt-Doped Kocite^R Electrodes in H₃PO₄ Fuel Cells", MERADCOM Contract DAAG53-76-C-0014, Interim Technical Report, January, 1978.

1. Determining whether a better catalyst resulted from a production sequence of
 - a. Kocite material production - leaching - platinum impregnation, or
 - b. Kocite material production - platinum impregnation - leaching

Higher platinum dispersions were obtained using the first production sequence.

2. Determining whether platinum impregnation of leached Kocite material by chloroplatinic acid, platinum diamine-dinitrite, or platinum acetylacetonate gives higher platinum dispersion. The best platinum dispersions were obtained with platinum diaminedinitrite. Electrodes are being fabricated from Kocite electrocatalysts made by this technique to determine if improved fuel cell performance is obtained.

Kocite electrode production during the previous contract period was aimed at the following goals:

1. Establishing that very high-surface-area Kocite electrocatalysts produced from leached Kocite materials could be successfully incorporated into PTFE-bonded gas-diffusion electrodes for use in phosphoric-acid-electrolyte fuel cells,
2. Determining the general electrode structure required to give good performance results with these electrocatalysts, and
3. Determining whether ERC machine rolled or sheet mold electrode production techniques gave clearly superior results.

Kocite electrode (cathode) performance data clearly indicated that electrodes fabricated from Kocite electrocatalysts prepared from leached Kocite materials gave better results than those fabricated from unleached Kocite materials. These Kocite electrodes were shown to perform stably for at least 4500 hrs. Similar results were obtained using both machine rolled and sheet mold Kocite electrodes. The performance levels shown in Table II were obtained using $\sim 0.6 \text{ mg/cm}^2$ Pt-loaded Kocite electrodes as cathodes versus 2 mg/cm^2 Pt-black anodes at atmospheric pressure and 180°C .³

Table II

Best 1977 Cell Performance Results

Current Density (ma/cm^2)	100	200
Terminal Cell Voltage (V)	0.66-0.68	0.60-0.62
Oxygen Gain (mV)	65	75

1.4 Program for the Past Six Month Period

The primary effort during this period was the preparation of large Kocite electrocatalyst batches (50-250 g) to provide enough material for both electrode structure optimization and a determination of Kocite electrode performance reproducibility. The main efforts of the last six months have been in the following areas:

(A) Preparation and Leaching of Kocite Materials

The leaching parameters of Kocite materials were standardized and the leaching process scaled up to produce 100-125 g batches of leached Kocite material.

(B) Kocite Electrocatalyst Production

All steps in the platinum impregnation of leached Kocite materials were scaled up to allow the production of 100-150 g electrocatalyst batches. Both chloroplatinic acid and platinum diamine-dinitrite impregnation techniques were used to produce Kocite electrocatalysts with good platinum dispersions. The micropore structure and particle shape were examined for a number of electrocatalysts using both nitrogen desorption isotherms and Transmission Electron Microscopy.

(C) Kocite Electrode Fabrication

Several Kocite electrocatalysts were delivered to ERC for incorporation into fuel cell electrodes. Roughly an equal number of machine rolled and sheet mold electrodes were produced.

(D) Kocite Electrode Testing

For the first time during this program, Kocite electrodes were routinely used as both cathodes and anodes in the same cell. Prior to this $2 \text{ mg}/\text{cm}^2$ Pt-black counter electrodes were used.

Much of the testing performed during this period was aimed at determining the reproducibility of Kocite electrode cathode performance. Over 60 cells were tested at UOP and ERC.

A detailed discussion of the results obtained in each of these areas is presented in the following sections.

II. PREPARATION AND LEACHING OF KOCITE MATERIALS

2.1 Kocite Materials

The preparation of the Kocite materials used during the present contract period is reported in this section. In almost all cases Alcoa's Hydral 705 alumina substrate was used with a benzene pyro-polymer precursor. Some of the preparation conditions as well as some of the chemical and physical properties of these Kocite materials are listed in Table III. Besides the Hydral 705 based Kocite materials, Kocite materials made with either Kaiser substrate alumina or Cabot's Alon alumina are also listed. A comparison of the properties of these Kocite materials produced using different alumina substrates will be made later. As indicated in section 1.3, standard Kocite materials for this program are produced from the Hydral 705 alumina substrate, having a carbon content of about 25 wt-%. For Kocite materials using either a Kaiser or Alon alumina substrate, similar surface areas can be obtained with carbon contents of 40-50 wt-%. The Kaiser based materials have a particle size of $\sim 2 \mu\text{m}$, larger than the $\sim 0.5 \mu\text{m}$ particle size of the Hydral based materials, causing increased diffusion losses in a fuel cell electrode compared to the Hydral based materials. The Alon based materials have a much smaller particle size ($\sim 0.05 \mu\text{m}$) and have yet to be evaluated in a fuel cell electrode.

Nitrogen desorption measurements have been used during this program to characterize the pore volume distribution (PVD) of both the Kocite material and the resulting electrocatalyst. The difference in pore volume distribution of Kocite materials attainable by a simple variation of the alumina substrate is shown in Figure 1, where the PVD's of typical Hydral 705, Kaiser and Alon based Kocite materials are shown. Kaiser based material has a relatively broad pore volume distribution while Hydral 705 based Kocite material has a distribution sharply peaked near 4.0 nm. Alon based Kocite material has a peak near 3.0 nm but also a substantial number of pores with diameters greater than 10 nm.

Table III
Characteristics of Kocite^R Materials

<u>Batch Number</u>	3380-65	3289-120	3576-60	3648-9	3648-32
<u>Preparation</u>					
Substrate	Kaiser	Hydral 705	Hydral 705	Hydral 705	Hydral 705
Pyropolymer Precursor	C ₆ H ₆	C ₆ H ₆	C ₆ H ₆	C ₆ H ₆	C ₆ H ₆
Pyrolysis Temperature (°C)	900	840	865	850	850
<u>Characteristics</u>					
Carbon Content (Wt-%)	42.2	21.52	25.33	25.54	26.53
Resistivity, ρ , @ 25°C (Ω -cm)	0.006	0.17	0.14	0.079	0.064
Apparent Bulk Density (g/ml)	0.85	0.30	0.278	0.32	0.31
Surface Area (m ² /g)	64	107	123	63	53
Pore Volume (ml/g)	0.17	0.15	0.17	0.09	0.08
Average Pore Diameter (nm)	10.7	5.6	5.5	5.7	6.0
Pore Volume Distribution Measured	Yes	Yes	No	No	No
Mean Particle Size (μ m)	2	60.5	60.5	60.5	60.5

Table III (Continued)
Characteristics of Kocite^R Materials

<u>Batch Number</u>	3648-54	3648-66	3648-68	3648-88	3648-104	3648-110	3648-118
<u>Preparation</u>							
<u>Substrate</u>	Hydral 705	Hydral 705	Hydral 705	Hydral 705	Alon Alumina	Hydral 705	Hydral 705
<u>Pyropolymer Precursor</u>	C ₆ H ₆	C ₆ H ₆	C ₆ H ₆	C ₆ H ₆	C ₆ H ₆	C ₆ H ₆	C ₆ H ₆
<u>Pyrolysis Temperature (°C)</u>	843	835	842	840	905	842	840
<u>Characteristics</u>							
<u>Carbon Content (Wt-%)</u>	25.65	24.30	25.31	23.65	48.87	21.91	25.31
<u>Resistivity, ρ, @ 25°C (Ω-cm)</u>	0.089	0.064	0.081	0.110	0.024	0.120	0.127
<u>Apparent Bulk Density (g/ml)</u>	0.30	0.29	0.30	0.32	0.16	0.31	0.32
<u>Surface Area (m²/g)</u>	73	73	81	65	74	86	92
<u>Pore Volume (ml/g)</u>	0.10	0.11	0.10	0.09	0.14	0.12	0.12
<u>Average Pore Diameter (nm)</u>	5.5	6.0	4.9	5.5	7.6	5.6	5.2
<u>Pore Volume Distribution Measured</u>	Yes	No	No	No	Yes	No	No
<u>Mean Particle Size (μm)</u>	~0.5	~0.5	~0.5	~0.5	~0.05	~0.5	~0.5

Transmission Electron Micrographs (TEM) were made of each type of Kocite material.⁴ Typical micrographs are shown in Figures 2, 3 and 4. The micrograph of the Hydral 705 based Kocite material (Figure 2) clearly shows this Kocite material consists of hexagonally shaped platelets with particle dimensions of ~ 100 to 500 nm in both length and width, and ~ 10 nm in thickness. A comparison of these micrographs with micrographs of the Hydral 705 alumina indicates no change in particle shape and no apparent change in particle structure occurs during pyropolymer deposition. The Kaiser based Kocite particles shown in Figure 3 are clearly both substantially larger and less regular than the Hydral 705 based Kocite particles shown in Figure 2. In contrast, the Alon based Kocite particles shown in Figure 4 are much smaller and have a narrow particle size distribution.

2.2 Leaching of Kocite Materials

In order to produce the pyropolymer structure which serves as the support for the small platinum particles of a Kocite electrocatalyst, the alumina substrate is leached from the Kocite material using phosphoric acid. At the start of the current contract period the standard process involved leaching the alumina at 135 - 140°C for about 24 hrs. This leaves a residual aluminum content in the leached Kocite material as high as 0.3 wt-%. To further reduce the aluminum content, which might degrade electrocatalyst performance in a fuel cell, the leaching temperature was raised to 180°C for a 20 hour period. With a starting Hydral 705 based Kocite material having a surface area of $80\text{ m}^2/\text{g}$, the resultant leached material has a surface area about $700\text{ m}^2/\text{g}$. Current production conditions and typical leached Kocite material properties are summarized in Table IV.

At the beginning of the contract period a 5 liter flask apparatus was used for the leaching process. The flask accepted a 175 g Kocite batch charge and produced ~ 40 g of leached Kocite. This facility was scaled up to accommodate a 12 liter flask allowing the use of a 420 g charge of the standard Hydral 705-based Kocite material. About 100 to 150 g of leached Kocite material is produced per batch.

The characteristics of the leached Kocite materials used in electrocatalyst preparation during the current contract period are listed in Table V. Leached Kocite materials are denoted by the addition of an "L" following the Kocite batch identification number. With two exceptions, the leached Kocite materials listed in this table were produced from Hydral 705 based Kocite materials. With this material an approximately 9 fold increase in surface area per gram is obtained by removing the alumina substrate. For the Kaiser and Alon based Kocite materials the

⁴TEM results obtained with the cooperation of Professor A. V. Crewe and Mitsuo Ohtsuki at the University of Chicago.

Figure 1

Nitrogen Desorption Pore Volume
Distributions for Kocite Materials
From Hydral 705 Alumina (3648-54),
Kaiser Substrate Alumina (3576-65),
and Alon Alumina (3648-104).

PORE VOLUME DISTRIBUTION

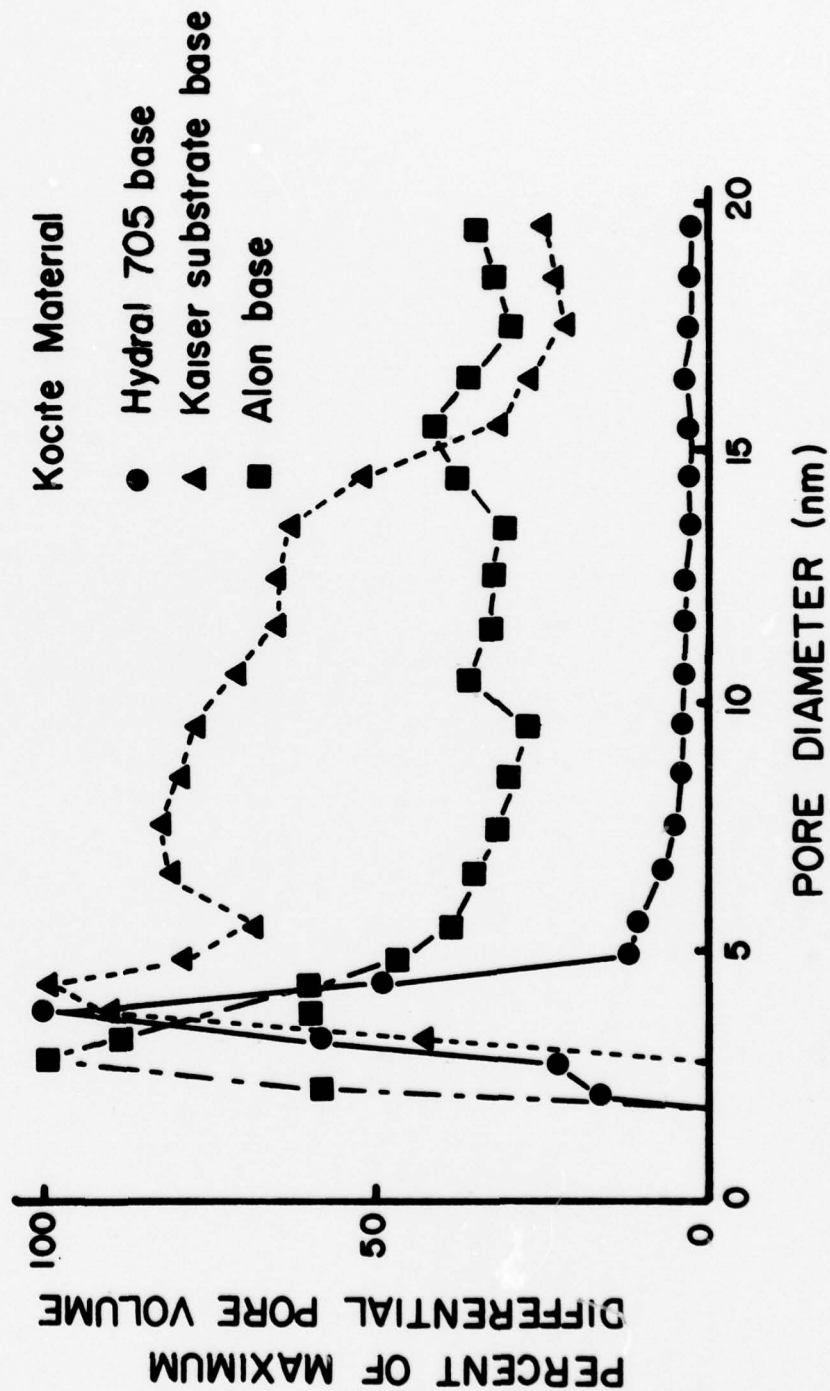


Figure 2

Transmission Electron Micrograph of
Kocite Material 3648-94 Made From
Hydral 705 Alumina
100 nm



Figure 3

Transmission Electron Micrograph of
Kocite Material 3173-133 Made From
Kaiser Substrate Alumina

100 nm



Figure 4

Transmission Electron Micrograph of
Kocite Material 3648-104 Made From

Alon Alumina

100 nm

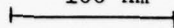


Table IV

Production of Leached Kocite Materials

Production Conditions

15 ml of 85% H_3PO_4 per gram of Kocite materials

180°C for 20 hrs.

Characterization of Material

Surface Area

$\sim 700 \text{ m}^2/\text{g}$

Phosphorous Content

$\sim 1\%$

Aluminum Content

$\sim 0.12\%$

Table V

Leaching Parameters of Kocite^R Materials

<u>Batch Number</u>	3289-120L	3576-60L	3648-32L	3648-54L	3648-66L	3648-68L	3648-88L
<u>Preparation</u>							
Kocite Material Used	3289-120	3576-60	3648-32	3648-54	3648-66	3648-68	3648-88
Leaching Temperature (°C)	140	142	161	181	179	180	181
Leaching Time (Hrs)	24	24	18	24	24	20	20
<u>Characterization</u>							
Carbon Content (Wt-%)			91.56	88.70	92.66	92.37	94.52
Resistivity, ρ , @ 25°C (Ω -cm)	0.107	0.166					
Surface Area (m^2/g)	989	881	585	579	655	645	668
Pore Volume (ml/g)	1.76	1.57	1.02	1.05	1.29	1.17	1.24
Average Pore Diameter (nm)	7.1	7.1	7.0	7.3	7.9	7.3	7.4
Pore Volume Distribution Measured	No	No	Yes	Yes	No	No	No

Table V (Continued)

Leaching Parameters of Kocite^R Materials

Batch Number	3648-9L	3648-110L	3648-104L	3380-65L	3648-115L	3648-118L
<u>Preparation</u>						
Kocite Material Used	3648-9	3648-110	3648-104	3380-65	Combined 3648-9L + 3648-110L	3648-118
Leaching Temperature (°C)	181-182	180	180	181	-	180
Leaching Time (Hrs)	20	20	20	21	-	20
<u>Characterization</u>						
Carbon Content (Wt-%)	96.16	91.74	90.32	89.06		90.78
Resistivity, ρ , @ 25°C (Ω -cm)						
Surface Area (m^2/g)	635	785	267	386		815
Pore Volume (ml/g)	1.14	1.46	0.59	0.90		1.45
Average Pore Diameter (nm)	7.2	7.4	8.8	9.3		7.1
Pore Volume Distribution Measured	No	No	Yes	Yes	No	No

increase in surface area is less dramatic, the leached Kaiser based material having a 6.5 fold increase to $386 \text{ m}^2/\text{g}$ and the leached Alon based material having a 4.5 fold increase to $267 \text{ m}^2/\text{g}$. The different surface area increases for the various types of leached material reflect the differing carbon content and pore structure of the starting Kocite materials.

For each type of leached Kocite material pore volume distributions are shown in Figures 5, 6 and 7 and compared with the PVD's of the starting Kocite materials. As shown in Figure 5, the pore sizes for the Hydral 705 based Kocite material increase after leaching but remains sharply peaked with the PVD peak moving from ~ 4.0 to ~ 6.0 nm. In the case of the Kaiser based material the PVD remains broad after leaching, although it is somewhat narrower with most of the pores having diameters less than 10 nm as shown in Figure 6. The Alon based material shows the most dramatic change. As shown in Figure 7, the PVD narrows dramatically and is sharply peaked near 6.0 nm. In particular, the relative volume of pores with diameters greater than 10.0 nm is greatly reduced. A comparison of the PVD's of the three different types of leached material is shown in Figure 8. The PVD's of the leached Hydral 705 and Alon based Kocite materials are quite similar suggesting that these materials may provide an electrocatalyst support having similar performance characteristics except for a possible reduction in cathode diffusion losses as a result of the substantially smaller particle size and increased particle size uniformity of the leached Alon based Kocite material.

III. KOCITE ELECTROCATALYSTS

3.1 Kocite Electrocatalyst Preparation

During the present contract period, electrocatalyst batch size was scaled up to 50-150 g with the intent of producing fewer Kocite electrocatalyst batches, but with impregnation techniques identified as producing good electrocatalysts in small batch sizes. Preparation details and physical properties of Kocite electrocatalysts prepared during the present contract period are listed in Tables VI and VII.

Details relating to the platinum impregnation of leached Kocite materials are given in Table VI. As indicated, most impregnations were made using chloroplatinic acid (CPA) with a water solvent. However three platinum diaminedinitrite (PDD) impregnations were made using different reduction atmospheres. The most important batches and conclusions drawn from their analysis are summarized as follows:

- (A) A large standard batch (3648-94A) was prepared to allow ERC to have an adequate amount of electrocatalyst to perform an extensive electrode structure optimization study, which is currently in progress. This batch was produced by combining electrocatalyst batches 3648-66A and 3648-68A.

Figure 5

Nitrogen Desorption Pore Volume
Distribution for Kocite Material
3648-54 and Leached Kocite
Material 3648-54L.

PORE VOLUME DISTRIBUTION

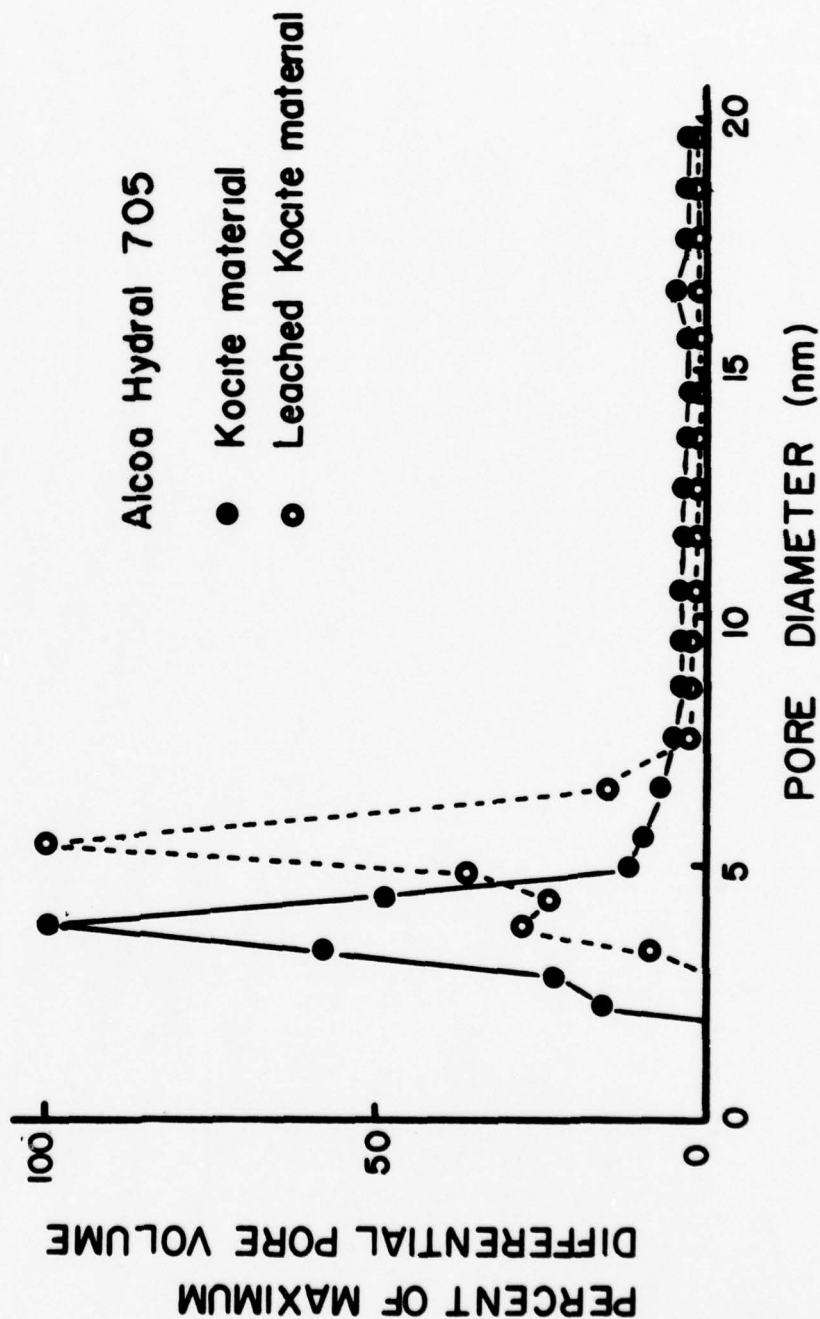


Figure 6

Nitrogen Desorption Pore Volume
Distribution for Kocite Material
3576-65 and Leached Kocite
Material 3576-65L.

PORE VOLUME DISTRIBUTION

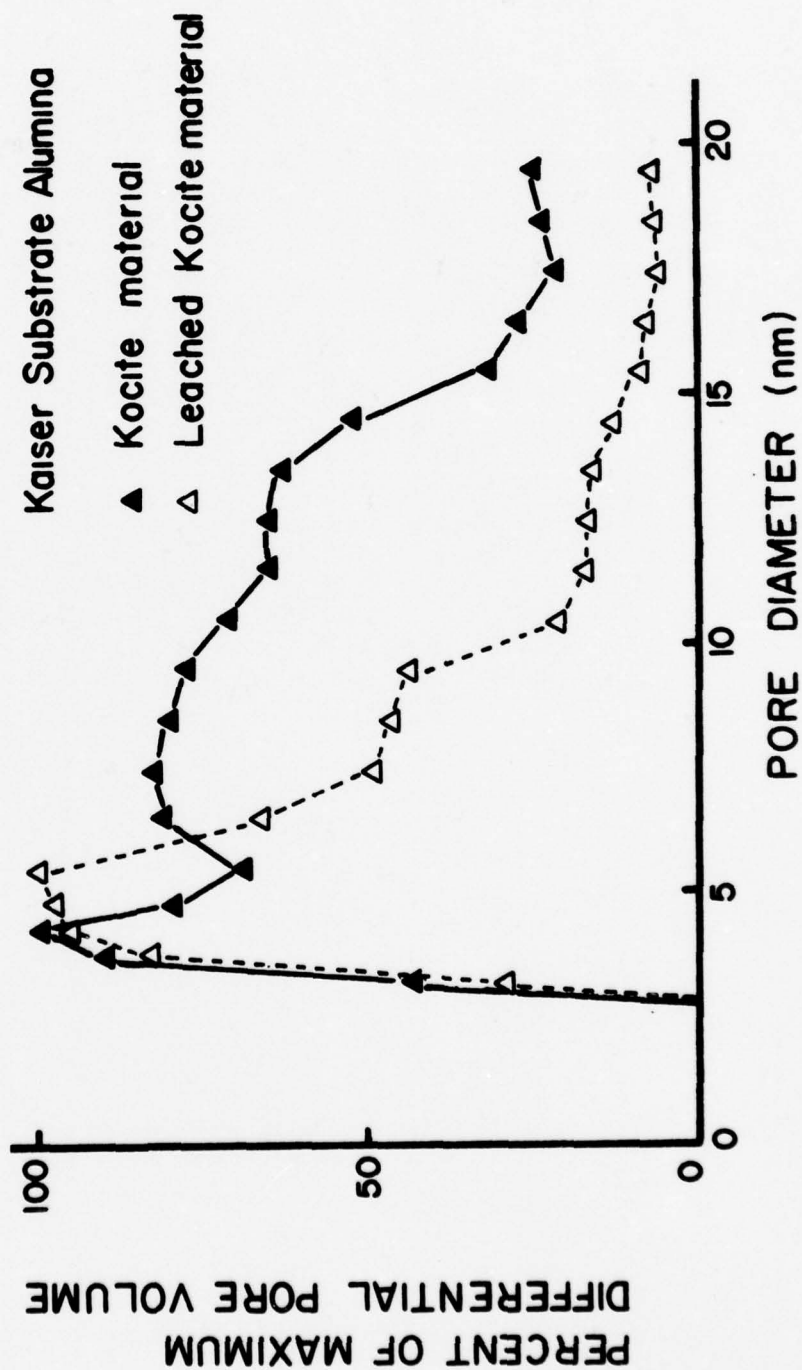


Figure 7
Nitrogen Desorption Pore Volume
Distribution for Kocite Material
3648-104 and Leached Kocite
Material 3648-104L.

PORE VOLUME DISTRIBUTION

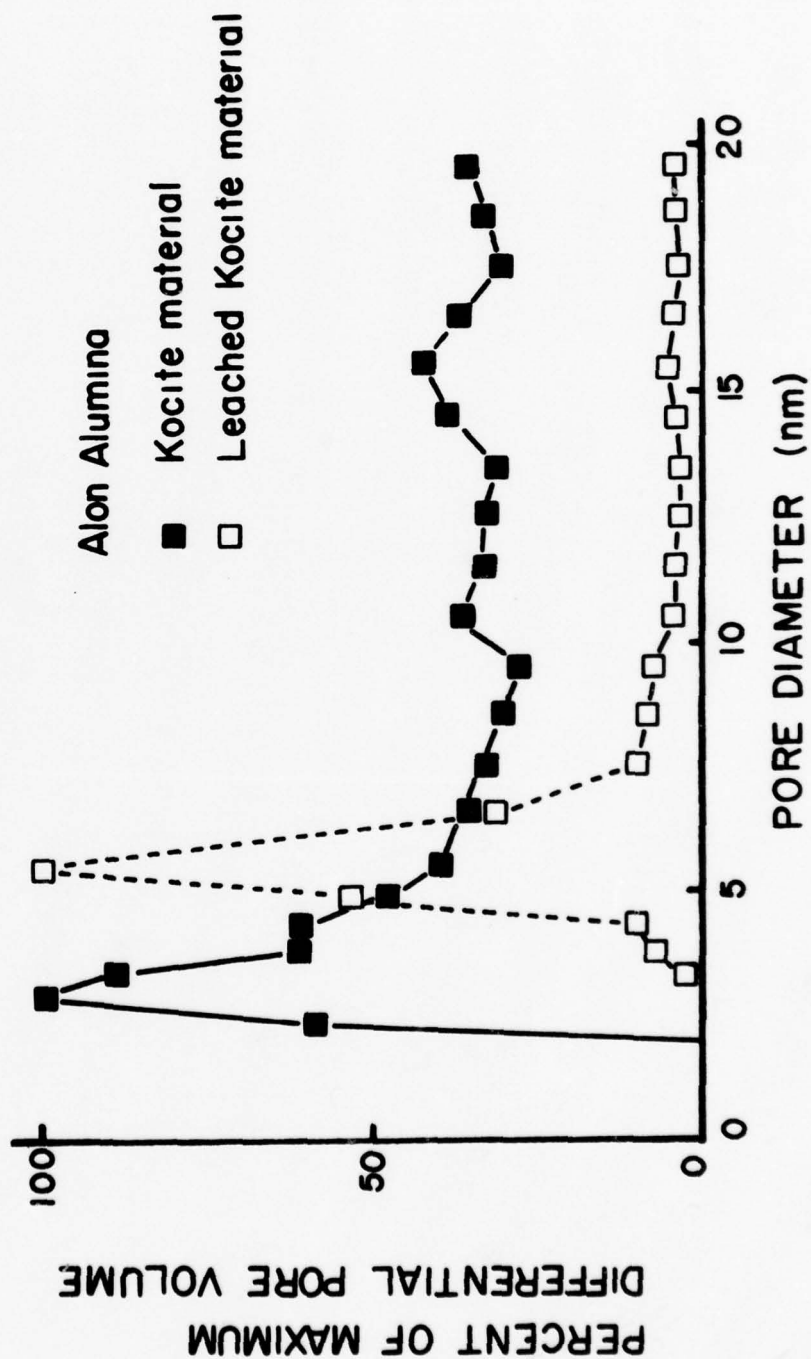


Figure 8

Nitrogen Desorption Pore Volume
Distribution for Leached Kocite
Materials from Hydral 705 Alumina
(3648-54L), Kaiser Substrate
Alumina (3576-65L), and Alon
Alumina 3648-104L.

PORE VOLUME DISTRIBUTION

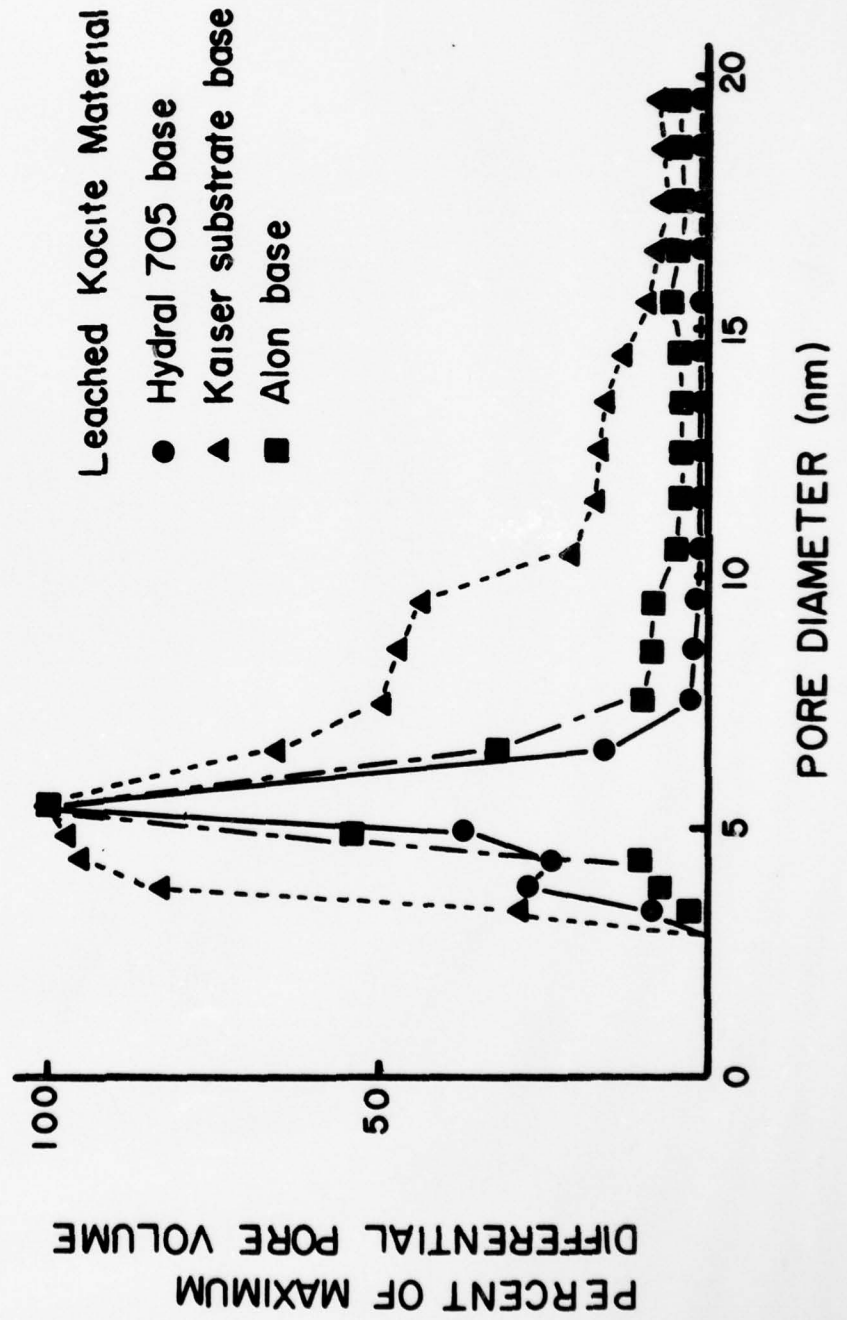


Table VI

Platinum Impregnation of Kocite^R Materials

Batch Number	3289-127A	3576-61A	3576-61B	3648-32A	3648-32AR	3648-54A	3648-54AR	3648-66A	3648-68A
Preparation									
Kocite Material Used	3289-120L	3576-60L	3576-60L	3648-32L	3648-32A	3648-54L	3648-54A	3648-66L	3648-68L
Platinum Source*	CPA	PDD	CPA	CPA	-	CPA	-	CPA	CPA
Solvent	C ₂ H ₅ OH	H ₂ O	H ₂ O	H ₂ O	-	H ₂ O	-	H ₂ O	H ₂ O
Reduction Atmosphere	H ₂	H ₂	H ₂	N ₂	H ₂	N ₂	H ₂	H ₂	H ₂
Reduction Temperature (°C)	260	260	260	263	240	230	230	260	260
Reduction Time (Hrs)	2.0	2.0	2.0	2	1	2	1 1/4	2	2
Characteristics									
Batch Size (g)	60	10	10	144	69	110	110	105	113
Platinum Concentration, (Wt-%)	17.3	11.4	16.3	15.2	15.2	16.7	15.7	15.7	15.8
Surface Area (m ² /g)	661	620		531		542	604	625	
Pore Volume (ml/g)		1.07		0.93		1.09	1.29	1.22	
Average Pore Diameter (nm)		6.9		7.0		8.0	8.5	7.8	
Pore Volume Distribution Measured	Yes	No	No	Yes	No	Yes	Yes	Yes	Yes

*CPA = chloroplatinic acid; PDD = platinum diaminedinitrite.

Table VI (Continued)

Platinum Impregnation of Kocite^R Materials

Batch Number	3648-94A	3648-88A	3648-115A	3648-104A	3648-65A	3648-115B	3648-115C	3648-118A
Preparation								
Kocite Material Used	-66A and -68A	3648-88L	3648-115L -9L and -110L	3648-104L	3380-65L	3648-115L -9L and -110L	3648-115L -9L and -110L	3648-118L
Platinum Source*	Made	CPA	PDD	CPA	CPA	PDD	PDD	CPA
Solvent	By	H ₂ O	1.0 M HNO ₃	H ₂ O	H ₂ O	1.0 M HNO ₃	1.0 M HNO ₃	H ₂ O
Reduction Atmosphere	Combining	H ₂	Air	H ₂	H ₂	N ₂	H ₂	H ₂
Reduction Temperature (°C)	Stated	260	275	260	260	260	260	260
Reduction Time (Hrs)	Batches	2	2	2	2	2	2	2
Characteristics								
Batch Size (g)	118	100	30	20	20	57	53	51
Platinum Concentration, (Wt-%)	15.5	16.6	31.15	16.7	15.6	16.4	16.8	10
Surface Area (m ² /g)	597	593	487	210	269	549	624	709
Pore Volume (ml/g)	1.19	1.02	0.90	0.48	0.59	0.92	1.09	1.24
Average Pore Diameter (nm)	8.0	6.9	7.4	9.1	8.8	6.7	7.0	7.0
Pore Volume Distribution Measured	Yes	No	No	No	No	No	No	No

*CPA = chloroplatinic acid; PDD = platinum diaminedinitrite.

Table VII

Characteristics of Kocite^R Electrocatalysts

Batch Number	Impregnation Technique	Batch Size (g)	Platinum Concentration (Wt-%)	Platinum X-Ray Analysis		Sent to ERC	Electrodes Fabricated
				Agglomeration ^a (%)	Particle Size ^b (nm)		
3289-127A	CPA	60	17.3	37	6.7		Yes
3576-61A	PDD	10	11.4	9	4.7		Yes
3576-61B	CPA	10	16.3	25	5.2		Yes
3648-32A	CPA	144	15.2	17	16.0	130 g	Yes
3648-32AR		74.1	15.2	29	13.5	69 g	Yes
3648-54A	CPA		See 3648-54AR				
3648-54AR		120	16.7	26	7.5	110 g	Yes
3648-66A	CPA	105	15.7			See 3648-94A	
3648-68A	CPA	113	15.8	29	4.6	See 3648-94A	
3648-94A		218	15.5	34	5.0		
3648-88A	CPA	105	16.6	32	4.9	213 g	Yes
3648-104A	CPA	20	16.7	48	5.9		
3380-65A	CPA	20	15.6	59	6.5		
3648-118A	CPA	51	10	16	4.2	45 g	
3648-115A	PDD	30	31.15	43	9.6		
3648-115B	PDD	56	16.4	41	15.5		
3648-115C	PDD	53	16.8	37	2.7	50 g	

^aThese results are standardized as discussed in Reference 1 with Kocite electrocatalyst 3576-66A used as a standard.

^bMean size of crystallites over 2.5 nm diameter.

Originally, electrocatalyst batches 3648-32A and 2648-54A were intended for this purpose, but it was discovered that they had been accidentally reduced in nitrogen. Upon subsequent reduction in hydrogen, the platinum particle size was larger than desired, so other electrocatalyst batches were used.

- (B) The effect of leaching temperature on the subsequent electrocatalyst platinum particle size was studied by comparing the platinum particle sizes of electrocatalysts 3289-127A and 3576-61B, prepared during the last contract period³, with batches 3648-66A and 3648-68A. The former materials were prepared with a 140°C leaching treatment, while the latter materials were leached at 180°C. A comparison of the platinum particle sizes of these electrocatalysts shown in Table VII indicates there is no discernible dependence of the platinum particle size on leaching temperature of the starting Kocite material.
- (C) To determine if a higher platinum dispersion could be obtained by improved wetting of the leached Kocite material during impregnation, electrocatalyst 3648-88A was sonically stirred and remained in an aqueous state for 72 hours. As indicated in Table VII, no improvement in platinum particle size was obtained.
- (D) To determine if a leached Alon based Kocite material would make a good electrocatalyst support, electrocatalyst 3648-104A was prepared. While the platinum particle size is larger than obtained with the leached Hydral 705 based materials, it is believed that an improved platinum dispersion is attainable with a starting Kocite material having a lower carbon content.
- (E) Three Kocite electrocatalyst batches were made with PDD impregnations and H₂, N₂ or air reductions. The smallest platinum particle size was obtained with the H₂ reduction. This electrocatalyst will be fabricated into electrodes.

In general Kocite electrocatalysts were prepared with 15 wt-% platinum. Exceptions to this platinum loading level are batch 3648-115A where air reduction oxidized about half the pyropolymer support, and batch 3648-118A, prepared at a level of 10 wt-% for improved platinum dispersion.

3.2 Kocite Electrocatalyst Structure

The particle shape, platinum particle size, platinum particle distribution, and pore volume distribution of several Kocite electrocata-

lysts were characterized by PVD and TEM studies. Within experimental error, the PVD of a leached Kocite material and the resulting Kocite electrocatalyst are identical. As a result no PVD results on electrocatalysts will be reported.

TEM studies made on several Kocite electrocatalysts prepared by CPA impregnation techniques indicate that the features elucidated by this technique are quite similar from electrocatalyst to electrocatalyst. The most important conclusions can be summarized by referring to Figures 9 and 10, TEM's which are typical of Kocite electrocatalysts as currently produced. In Figure 9, both the platinum particles (dark spots) and the porous nature of a Kocite electrocatalyst particle are clearly visible. Of particular interest in this figure are the distribution and size of the platinum particles. While the platinum dispersion is good over most of this particle, the area in the upper left hand corner contains a number of large (>10 nm dia) platinum particles. The existence of these large platinum particles clearly indicates the platinum impregnation technique is not optimized and implies that improved fuel cell performance is attainable when a more uniform, more highly dispersed platinum distribution can be produced.

The porosity and pore structure of Kocite electrocatalyst particles are clearly demonstrated in the TEM of Figure 10. The diameter of the pores shown in this figure are mostly in the 5.0-10.0 nm range, consistent with the PVD results in Figures 4 or 8. While platinum particle placement on the leached Kocite support is difficult to determine from Figures 9 and 10, it is believed that higher resolution TEM will provide useful information in this area.

IV. ELECTRODE FABRICATION AND TESTING

4.1 Electrode Fabrication

During the last six month period, ERC has prepared Kocite electrodes by two separate techniques: 1) the standard ERC machine calendaring process used previously and described in earlier reports², and 2) an experimental process utilizing a sheet mold technique. Machine calendered (rolled) electrodes are fabricated by rolling a discrete catalyst layer and then pressure bonding this layer to a carbon fiber paper electrode substrate. In contrast, in the sheet mold process a catalyst-PTFE mixture is deposited directly onto the carbon fiber paper. Sintering conditions of both types of catalyst layers are similar to those described in previous reports.²

PTFE contents of both types of catalyst layers are typically between 40 and 50 wt-%. During the present contract period 40 and 45 wt-% PTFE contents were used. The lower loading was used to obtain peak electrode performance quickly at the risk of later electrode flooding. However, in contrast to electrodes made in the last contract

Figure 9

Transmission Electron Micrograph of
Kocite Electrocatalyst 3648-94A

25 nm

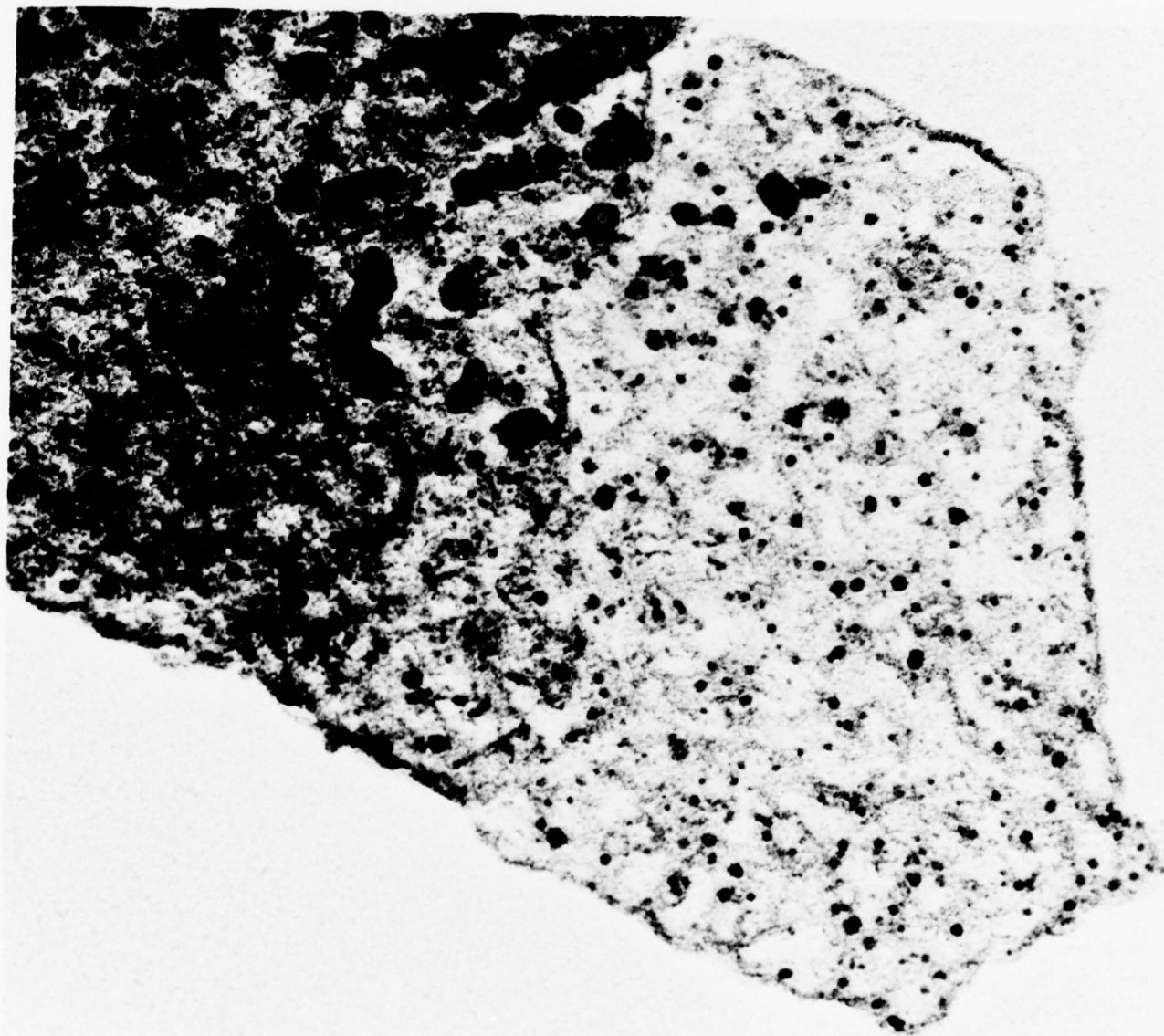
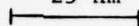
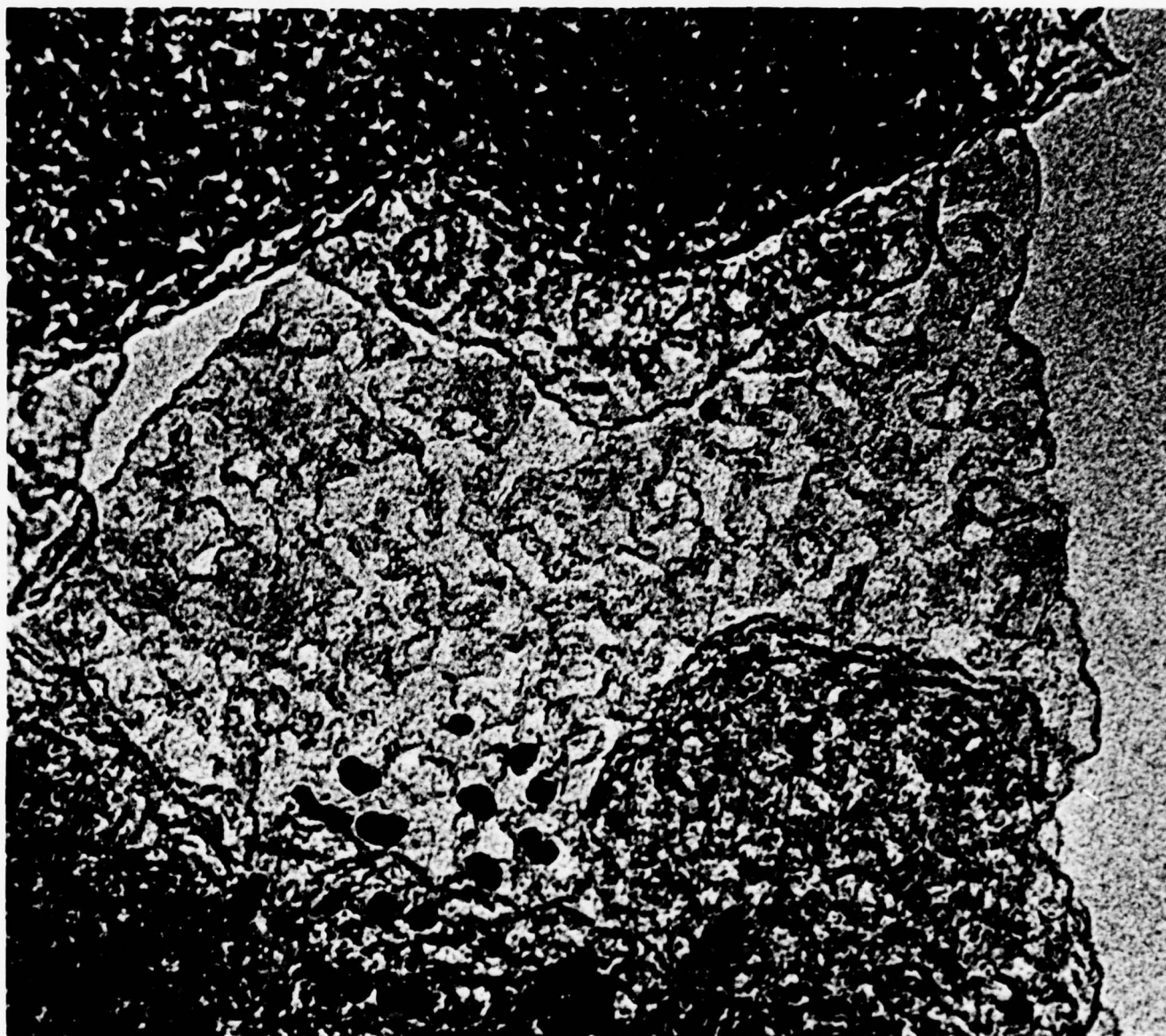


Figure 10

Transmission Electron Micrograph of
Kocite Electrocatalyst 3648-94A

25 nm



period at this PTFE loading, Kocite electrodes made at this PTFE loading during the present contract period appear to flood quickly, preventing stable cell performance. As a result a 45 wt-% PTFE loading was used during the latter part of the present contract period. The cause of this change in the behavior of 40 wt-% PTFE loaded Kocite electrodes is unclear but may result from; 1) changes in the electron fabrication process at ERC, particularly the mixing of Kocite electrocatalyst and PTFE powders, or 2) variations in the wettability of Kocite electrocatalysts as a result of the increased leaching temperature.

4.2 Cell Testing

Details of cell testing techniques and apparatus have been discussed in earlier reports.^{1,2,3} No changes in cell components were made during the present contract period. Cells were normally operated at 180°C using an ERC supplied Kynol matrix. In the few cases where Kocite electrodes were not used as both anode and cathode, a 2 mg/cm² Pt-black counter electrode was used. In contrast to the cell assembly procedure followed in previous contract periods, almost all cells were assembled without electrode prewetting. To standardize cell test procedures and operation with those currently in use at ERC, Mr. M. George of ERC visited the test lab at UOP to update UOP cell assembly personnel in cell assembly techniques.

V. RESULTS AND DISCUSSION

5.1 Introduction

In this section, the characteristics and performance of Kocite electrodes tested at UOP and ERC during the last six month contract period are presented. Where possible, the cell performance is correlated with Kocite electrocatalyst and Kocite electrode properties. The results obtained during the last six month period are summarized in section 5.3.

5.2 Cell Performance Results

The performance results of model phosphoric acid electrolyte fuel cells with Kocite electrodes are reported in this section. The characteristics of the Kocite electrodes and cell builds tested at ERC and UOP are listed in Tables VIII and IX respectively. A total of 61 cells were assembled and tested. The performance of all cells assembled during this period is listed in these tables with the exception of cells assembled with Kocite electrodes fabricated from incompletely reduced Kocite electrocatalysts. At ERC, Kocite electrodes fabricated

Table VIII

Kocite^R Electrode Characteristics - ERC

Cell Number	Kocite Electro catalyst Batch	Platinum Content (Wt-%)	Electrode Number	Nominal Platinum Loading (mg/cm ²)	PTFE Content (Wt-%)	Fabrication Method
ERC 149	3648-32AR	15.2	469B	~0.60	40	Sheet Mold
ERC 150	3648-32AR	15.2	469B	~0.60	40	Sheet Mold
ERC 151	3648-32AR	15.2	4697	~0.60	40	Sheet Mold
ERC 152	3648-54AR	16.7	4701	~0.65	40	Sheet Mold
ERC 153	3648-54AR	16.7	4701	~0.65	40	Sheet Mold
ERC 154	3648-54AR	16.7	4701	~0.65	40	Sheet Mold
ERC 155	3648-54AR	16.7	4911	~0.65	40	Sheet Mold
ERC 156	3648-54AR	16.7	4911	~0.65	40	Sheet Mold
ERC 157	3648-54AR	16.7	4976	~0.65	40	Machine Rolled
ERC 158	3648-54AR	16.7	4976	~0.65	40	Machine Rolled
ERC 159	3648-54AR	16.7	4702	~0.65	40	Sheet Mold
ERC 160	3648-94A	14.9	4912	~0.60	40	Sheet Mold
ERC 161	3648-94A	14.9	4912	~0.60	40	Sheet Mold
ERC 162	3648-94A	14.9	4914	~0.60	40	Sheet Mold
ERC 163	3648-94A	14.9	4914	~0.60	40	Sheet Mold
ERC 164	3648-94A	14.9	4914	~0.60	40	Sheet Mold
ERC 165	3648-94A	14.9	4912	~0.60	40	Sheet Mold
ERC 166	3648-94A	14.9	5049	~0.60	40	Sheet Mold
ERC 167	3648-94A	14.9	5050	~0.60	40	Sheet Mold
ERC 168	3648-54AR	16.7	5053	~0.65	45	Sheet Mold
ERC 169	3648-94A	14.9	4573	~0.55	45	Sheet Mold
ERC 170	3648-94A	14.9	4574	~0.55	45	Sheet Mold
ERC 171	3648-94A	14.9	4573	~0.55	45	Sheet Mold
ERC 172	3648-94A	14.9	5400	~0.60	45	Machine Rolled
ERC 173	3648-94A	14.9	5403	~0.65	45	Machine Rolled
ERC 174	3648-94A	14.9	4921	~0.55	45	Sheet Mold
ERC 175	3648-94A	14.9	4921	~0.55	45	Sheet Mold
ERC 176	3648-94A	14.9	5401	~0.65	45	Machine Rolled
ERC 177	3648-94A	14.9	5047	~0.60	45	Sheet Mold
ERC 178	3648-94A	14.9	5401	~0.65	45	Machine Rolled
ERC 179	3648-94A	14.9	5400	~0.60	45	Machine Rolled
ERC 180	3648-94A	14.9	5400	~0.60	45	Machine Rolled
ERC 181	3648-94A	14.9	5400	~0.60	45	Machine Rolled
ERC 182	3648-94A	14.9	5400	~0.60	45	Machine Rolled
ERC 183	3648-94A	14.9	5401	~0.65	45	Machine Rolled

Table IX
Kocite^R Electrode Characteristics - UOP

Cell Number	Platinum Concentration (Wt-%)	Electrode Number	Nominal Platinum Loading (mg/cm ²)	PTFE Content (Wt-%)	Fabrication Method
3648-54AR-1	16.7	4911	~0.65	40	Sheet Mold
3648-54AR-2	16.7	4911	~0.65	40	Sheet Mold
3648-54AR-3	16.7	4911	~0.65	40	Sheet Mold
3648-54AR-4	16.7	4701	0.60 ^a	40	Sheet Mold
3648-54AR-5	16.7	4701	0.60 ^a	40	Sheet Mold
3648-54AR-6	16.7	4701	0.60 ^a	40	Sheet Mold
3648-54AR-7	16.7	4977	~0.65	40	Machine Rolled
3648-54AR-8	16.7	4977	~0.65	40	Machine Rolled
3648-54AR-9	16.7	4977	~0.65	40	Machine Rolled
3576-61A-1*	11.4		0.36 ^a	40	Sheet Mold
3576-61A-2*	11.4		0.36 ^a	40	Sheet Mold
3576-61A-3*	11.4		0.36 ^a	40	Sheet Mold
3648-94A-1	14.9	5402	0.58 ^a	45	Machine Rolled
3648-94A-2	14.9	5402	0.58 ^a	45	Machine Rolled
3648-94A-3	14.9	5402	0.58 ^a	45	Machine Rolled
3648-94A-4	14.9	5402	~0.58	45	Machine Rolled
3648-94A-5	14.9	5403	~0.60	45	Machine Rolled
3648-94A-6	14.9	5403	~0.60	45	Machine Rolled

*Cells assembled with a 2 mg/cm² Pt-black counter electrode.

^a Electrode platinum loading measured by X-ray fluorescence.

from Kocite electrocatalyst batches 3648-32AR, 3648-54AR and 3648-94A were tested with the emphasis placed on testing Kocite electrodes from batch 3648-94A, the "standard" Kocite electrocatalyst batch. At UOP, Kocite electrodes were tested from batches 3648-54AR, 3648-94A and 3576-61A, a PDD impregnated electrocatalyst prepared during the previous contract period.

For the first time the electrode batch as well as electrocatalyst batch numbers are listed in Tables VIII and IX. This is done to allow the performance of particular electrode batches to be identified and compared with other electrode batches which may have been made under slightly differing conditions. Between two and four 5"x15" electrode sheets were prepared at the same time with the same process conditions. These electrode sheets are numbered sequentially. Thus electrode sheets 5400-5403 were made at the same time under the same conditions and would be expected to have nearly identical performance.

Nominal Kocite electrode platinum loadings are listed in Tables VIII and IX. These loadings were calculated from Kocite electrocatalyst platinum loadings. In some cases electrode platinum loadings were measured by X-ray fluorescence using a standard analyzed chemically for platinum content. Such measurements of a machine rolled electrode sheet indicated the actual platinum loading was within 3% of the calculated value with a variation of platinum loading across the electrode sheet of less than 5%. For sheet mold electrode sheets the variation in platinum loading may be somewhat larger, which could have a small but definite effect on the comparative performance of electrodes cut from the same electrode sheet. In Tables VIII and IX, calculated platinum loadings have been rounded off to the nearest 0.05 mg/cm². Loadings measured by X-ray fluorescence have a reproducibility of better than 2%.

The performance of cells assembled at ERC and UOP is summarized in Tables X and XI, respectively. Important test results are summarized as follows:

- (A) With the exception of the three cells assembled from Kocite electrodes incorporating Kocite electrocatalyst batch 3576-61A, Kocite electrodes from the same electrode batch were used as both the air cathode and H₂ anode. This procedure has the advantage of determining the utility of Kocite electrodes as both cathodes and anodes and allows a comparison of two Kocite electrodes as cathodes or anodes by simply reversing the gases fed to the electrodes.

Table X

Summary of ERC Cell Performance Results at 130°C

Cell Number	Kocite Electro-catalyst Batch	Nominal Platinum Loading (mg/cm ²)	Terminal Voltage (mV) @ 200 mA/cm ²				Days Tested	Peak Performance	Comments
			Air	Oxygen	Air	Oxygen			
ERC 149	3648-32AR	~0.60	625	690	530	610	7	1	Re-reduced catalyst
ERC 150	3648-32AR	~0.60	640	720	520	640	7	1	Re-reduced catalyst
ERC 151	3648-32AR	~0.60	640	700	530	610	13	1	Flooded with time
ERC 152	3648-54AR	~0.65	630	700	540	620	12	1	Flooded with time
ERC 153	3648-54AR	~0.65	630	690	510	610	5	2	Cross gas leak
ERC 154	3648-54AR	~0.65	640	700	550	620	14	2	Flooded with time
ERC 155	3648-54AR	~0.65	640	700	540	630	43	6	Slight flooding
ERC 156	3648-54AR	~0.65	670	730	600	670	48	20	Stable
ERC 157	3648-54AR	~0.65	650	710	570	640	16	14	Failed cross gas leak
ERC 158	3648-54AR	~0.65	680	700	565	620	9	1	Prefilled electrodes
ERC 159	3648-54AR	~0.65	650	700	500	600	13	1	Flooded with time
ERC 160	3648-94A	~0.60	610	680	500	600	2	1	Flooded
ERC 161	3648-94A	~0.60	620	680	520	600	2	1	Flooded with time
ERC 162	3648-94A	~0.60	640	700	540	600	14	1	Flooded with time
ERC 163	3648-94A	~0.60	650	710	560	630	13	1	Flooded with time
ERC 164	3648-94A	~0.60	630	690	520	600	11	1	Flooded with time
ERC 165	3648-94A	~0.60	570	650	460	570	2	1	Flooded
ERC 166	3648-94A	~0.60	620	695	525	620	6	1	Experimental electrode
ERC 167	3648-94A	~0.60	615	680	510	590	5	1	Experimental electrode
ERC 168	3648-54AR	~0.65	620	680	520	600	1	1	Experimental electrode
ERC 169	3648-94A	~0.55	640	700	560	630	12	1	Slight decay
ERC 170	3648-94A	~0.55	600	660	490	580	1	1	Slight decay
ERC 171	3648-94A	~0.55	630	685	540	615	3	1	Slight decay
ERC 172	3648-94A	~0.65	650	705	580	640	41	5	Stable
ERC 173	3648-94A	~0.65	640	700	550	620	40	2	Slight decay
ERC 174	3648-94A	~0.55	610	670	520	600	1	1	Slight decay
ERC 175	3648-94A	~0.55	640	700	560	640	40	1	Stable
ERC 176	3648-94A	~0.65	660	715	580	640	16	1	Decayed
ERC 177	3648-94A	~0.60	610	680	520	600	6	2	Stable
ERC 178	3648-94A	~0.65	570	645	560	625	1	1	Cross gas leak
ERC 179	3648-94A	~0.60	640	700	560	625	4	1	Decayed
ERC 180	3648-94A	~0.60	670	725	600	660	25	12	Stable
ERC 181	3648-94A	~0.60	600	670	510	585	1	1	Stable
ERC 182	3648-94A	~0.60	650	700	570	630	10	1	Decayed
ERC 183	3648-94A	~0.65	660	720	590	660	5	2	Stable

Table XI

Summary of UOP Cell Performance Results at 180°C

Cell Build Number	Nominal Platinum Loading mg/cm ²	Terminal Voltage (mV) @ 100 mA/cm ²		Terminal Voltage (mV) @ 200 mA/cm ²		Days Tested	Peak Performance	Comments
		Air	Oxygen	Air	Oxygen			
3648-54AR-1	~0.65	665	724	591	658	20	1 day	Flooded
3648-54AR-2	~0.65	606	693	495	624	19	7 days	Gas crossover
3648-54AR-3	~0.65	650	718	585	668	7	1 day	Flooded
3648-54AR-4	0.60 ^a	658	727	594	683	18	1 day	Run at 163°C, gas crossover
3648-54AR-5	0.60 ^a	646	727	571	675	7	1 day	Reverse polarized
3648-54AR-6	0.60 ^a	650		575		6	1 day	Flooded
3648-54AR-7	~0.65	624	713	545	650	18	1 day	Flooded
3648-54AR-8	~0.65	637		540		18	6 days	Stable
3648-54AR-9	~0.65	627	702	537	636	44	10 days	Stable
3576-61A-1*	0.36 ^a	595		488		18	8 days	Incorrect gaskets
3576-61A-2*	0.36 ^a	607	701	503	627	48	20 days	Stable
3576-61A-3*	0.36 ^a	611		515		14	4 days	Stable
3648-94A-1	0.58 ^a	668	729	595	664	42	36 days	Stable
3648-94A-2	0.58 ^a	658		576		28	2 days	Slight electrode misalignment
3648-94A-3	0.58 ^a	643		564		28	2 days	Incorrect gaskets
3648-94A-4	0.58 ^a	615	702	543	638	8	2 days	Unstable
3648-94A-5	~0.60	641	713	557	645	8	7 days	Stable
3648-94A-6	~0.60	645	710	577	661	8	1 day	Decayed

*Cells assembled with a 2 mg/cm² Pt-black counter electrode.^aElectrode platinum loadings measured by X-ray fluorescence.

- (B) The PTFE loading of Kocite electrodes was increased from 40 wt-% to 45 wt-% during this contract period as a result of the generally unstable performance and apparent rapid electrode flooding problems encountered at the lower PTFE loading. Since the PTFE loading of many stable Kocite cathodes tested during the last contract period was 40 wt-%, it is possible this problem is associated with changes in the Kynol matrix material, minor changes in the electrode fabrication process (particularly the sheet mold process), or minor changes in the electrocatalyst production process (increased leaching temperature). At 45 wt-% PTFE electrode flooding no longer appears to be a problem.
- (C) Based on the cell performance results obtained on cells with Kocite electrodes having 45 wt-% PTFE, machine rolled electrodes appear to provide a more reproducible performance than sheet mold electrodes. Further optimization of the sheet mold electrodes should improve the performance reliability of the sheet-mold electrodes.
- (D) From the data obtained on cell performance at UOP and ERC, two sets of cell builds merit discussion in attempting to determine the degree of reproducible cell performance attainable at this time with Kocite electrodes fabricated by ERC.
 - 1) Four cells (3648-54AR-1 to 4) were assembled at UOP as identically as possible under the supervision of Mr. M. George (ERC). While these cells apparently began flooding by the second or third day of operation, their performance level after several hours of operation is instructive as to the reproducibility and performance level which should be attainable for cells with Kocite electrodes having an improved structure. The performance data in Tables X and XI for electrodes from batch 3648-54AR represent values obtained after the first day of operation. The highest stable performance levels (air vs H₂) reached on the first day of operation are listed in Table XII for both normal and reversed operation at 180°C.

Table XII

First Day Performance Levels of
Cells 3648-54AR-1 to 4

<u>Cell Number</u>	<u>Terminal Voltage (mV) at 200 mA/cm², Air vs H₂</u>	
	<u>Normal</u>	<u>Reversed</u>
3648-54AR-1	591	570
3648-54AR-2	617	601
3648-54AR-3	597	597
3648-54AR-4	594	609

With the exception of the reversed operation level of the first cell, all cell performance levels were above 590 mV with an average performance level of 601 mV. These data suggest that reproducible Kocite electrode performance should be attainable with the proper electrode structure.

- ii) The Kocite electrode series from which the largest number of cells at UOP and ERC were assembled is the 5400-5403 series fabricated from electrocatalyst batch 3648-94A. A total of 15 cells were assembled and tested. Of these 15 cells, 12 had a stable performance level above 550 mV at 200 mA/cm² and 180°C. The performance of these cells is listed in Table XIII by electrode batch.

Table XIII

Performance Levels of Cell from Kocite
Electrode 5400-5403 Series

<u>Kocite Electrode Batch</u>	<u>Cell Number</u>	<u>Terminal Voltage (mV) at 200 mA/cm² (Air vs H₂)</u>	<u>Average Performance of Series at 200 mA/cm² (mV)</u>
5400	ERC-172	580	578
	ERC-179	560	
	ERC-180	600	
	ERC-182	570	

Table XIII (Continued)

Performance Levels of Cells from Kocite
Electrode 5400-5403 Series

<u>Kocite Electrode Batch</u>	<u>Cell Number</u>	<u>Terminal Voltage (mV) at 200 mA/cm² (Air vs H₂)</u>	<u>Average Performance of Series at 200 mA/cm² (mV)</u>
5401	ERC-176	580	585
	ERC-183	590	
5402	3648-94A-1	595	578
	3648-94A-2	576	
	3648-94A-3	564	
5403	ERC-173	550	561
	3648-94A-5	557	
	3648-94A-6	577	

The average performance of the 12 cells was 575 mV at 200 mA/cm². While considerable variation in cell performance still exists, the reproducibility of cell performance on cells assembled both at UOP and ERC appears to be considerably improved over that achieved during previous contract periods. At this time it is believed that the main causes of reproducibility problems are in cell assembly techniques and achieving an optimized Kocite cathode electrode structure.

- (E) Three cells were assembled at UOP using Kocite electrodes fabricated during the previous contract period from electrocatalyst batch 3576-61A. This batch was prepared by the PDD impregnation technique. The electrodes have a low Pt loading (~ 0.35 mg/cm²). These cells ran stably at 180°C with a best performance level of 611 mV at 100 mA/cm² and an average performance level of 605 mV at 100 mA/cm². At this low Pt-loading these results are quite encouraging and suggest that at ~ 0.6 Pt-loadings electrocatalysts produced by this technique should perform comparable to or better than CPA impregnated Kocite electrocatalysts.
- (F) To better characterize individual cell performance, polarization curve plots and lifetime data are shown in Figures 11-14. Polarization curves for cell 3648-94A-1 on air and

Figure 11

Polarization Curve for Cell 3648-94A-1
at 180°C. Platinum Loading 0.58 mg/cm².

Terminal Voltage

○ Air Cathode

● Oxygen Cathode

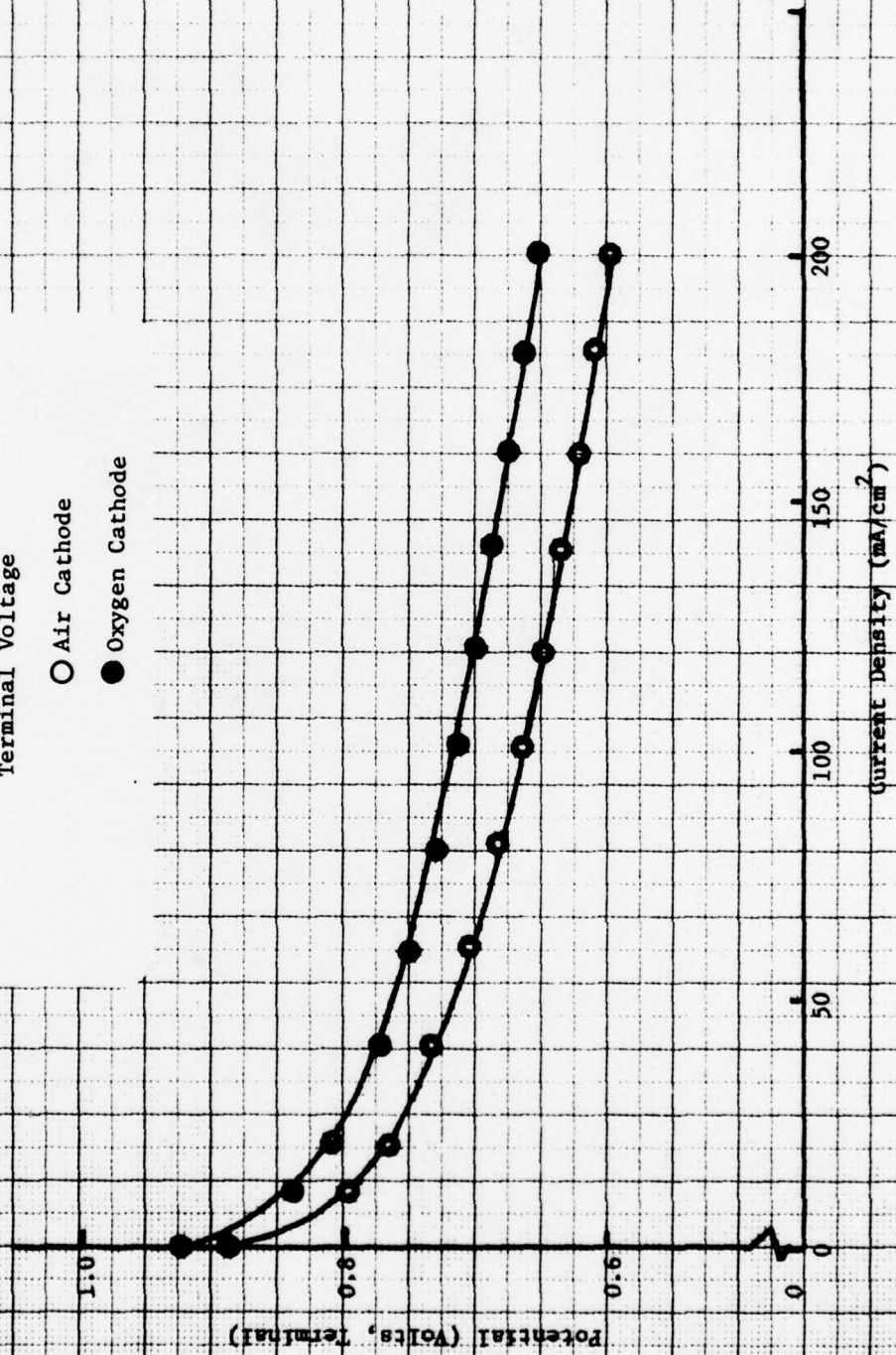


Figure 12

Lifetime Test for Cell 3643-94A-1 at 180°C.
Platinum Loading 0.58 mg/cm².

Terminal Voltage

● 100 mA/cm²

○ 200 mA/cm²

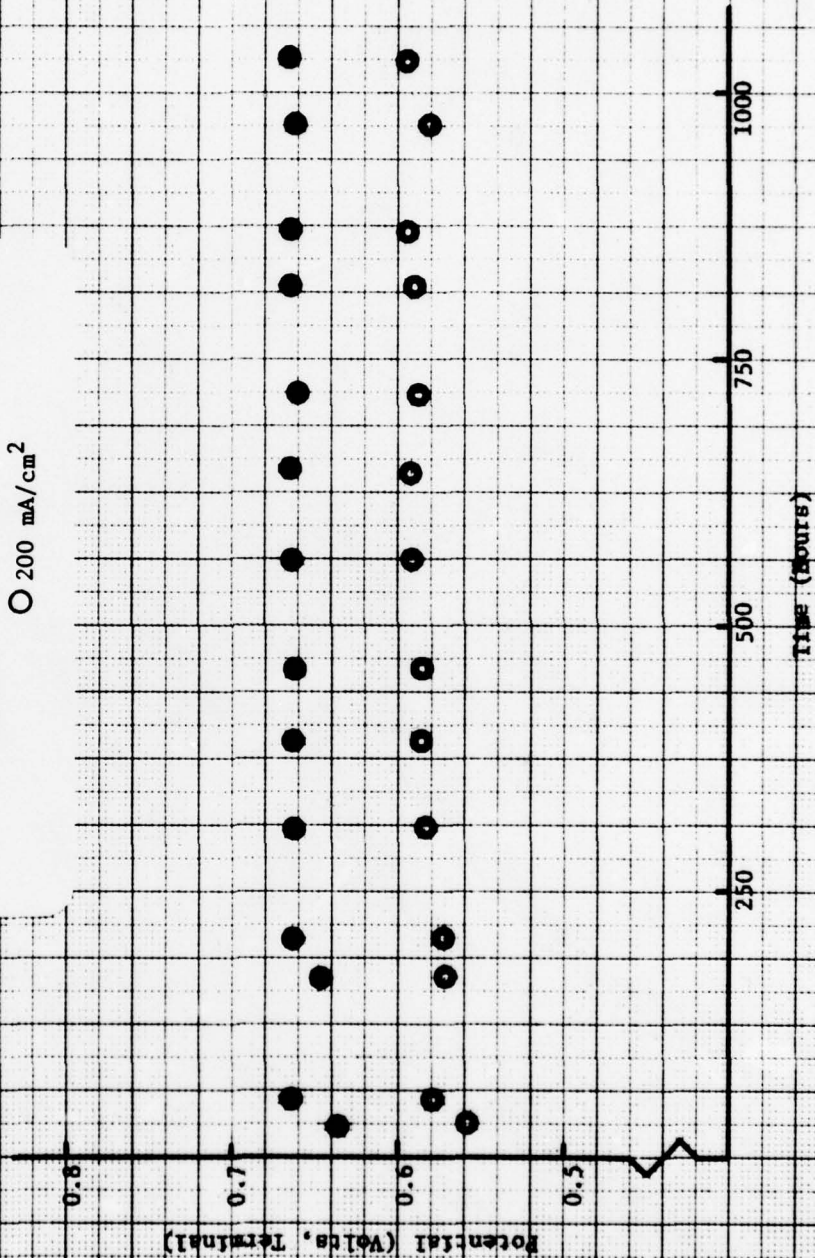


Figure 13

Polarization Curve for Cell ERC-180 at 180°C.
Platinum Loading 0.60 mg/cm².
Cell Resistance 14.6 mΩ.

Terminal Voltage

- Air Cathode
- Oxygen Cathode

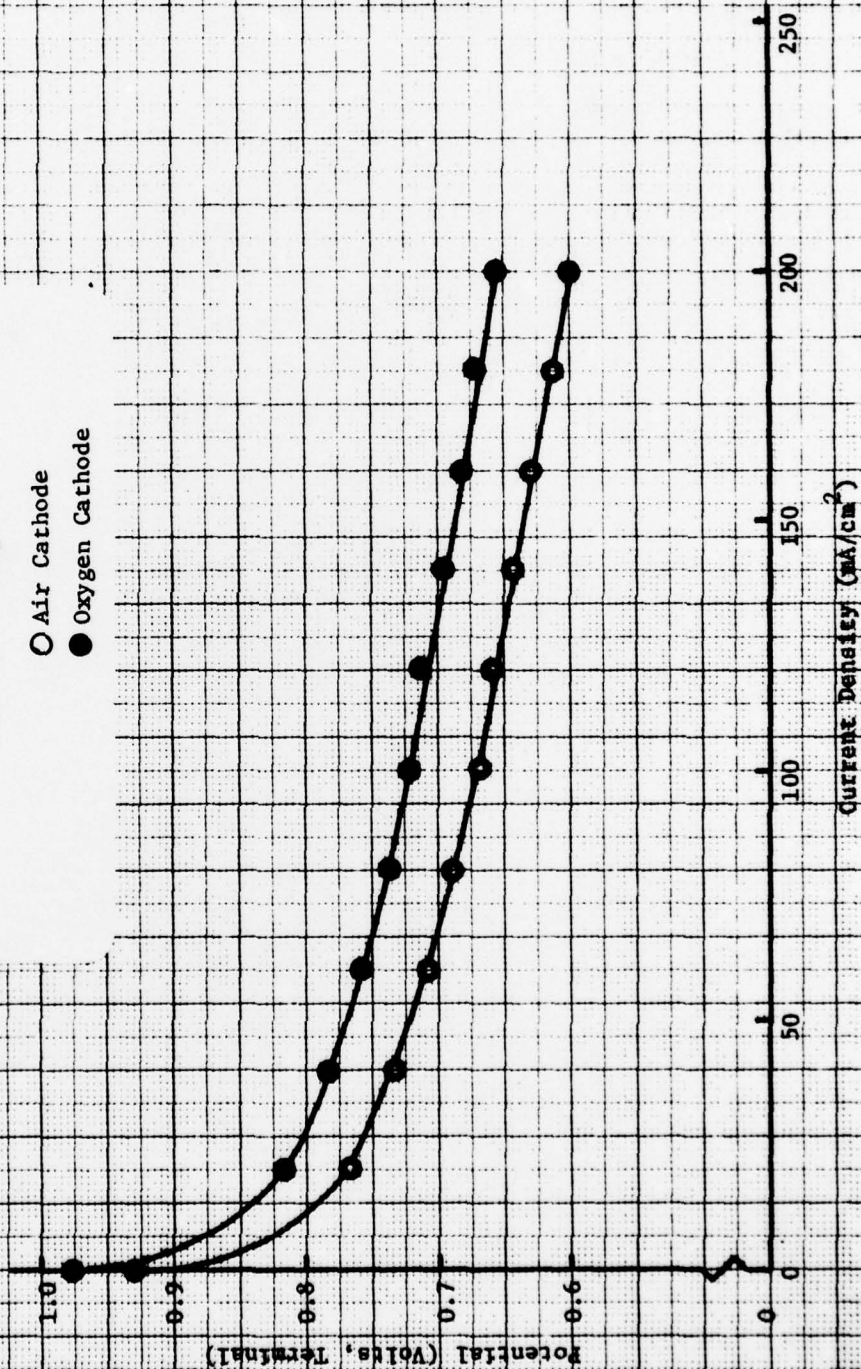
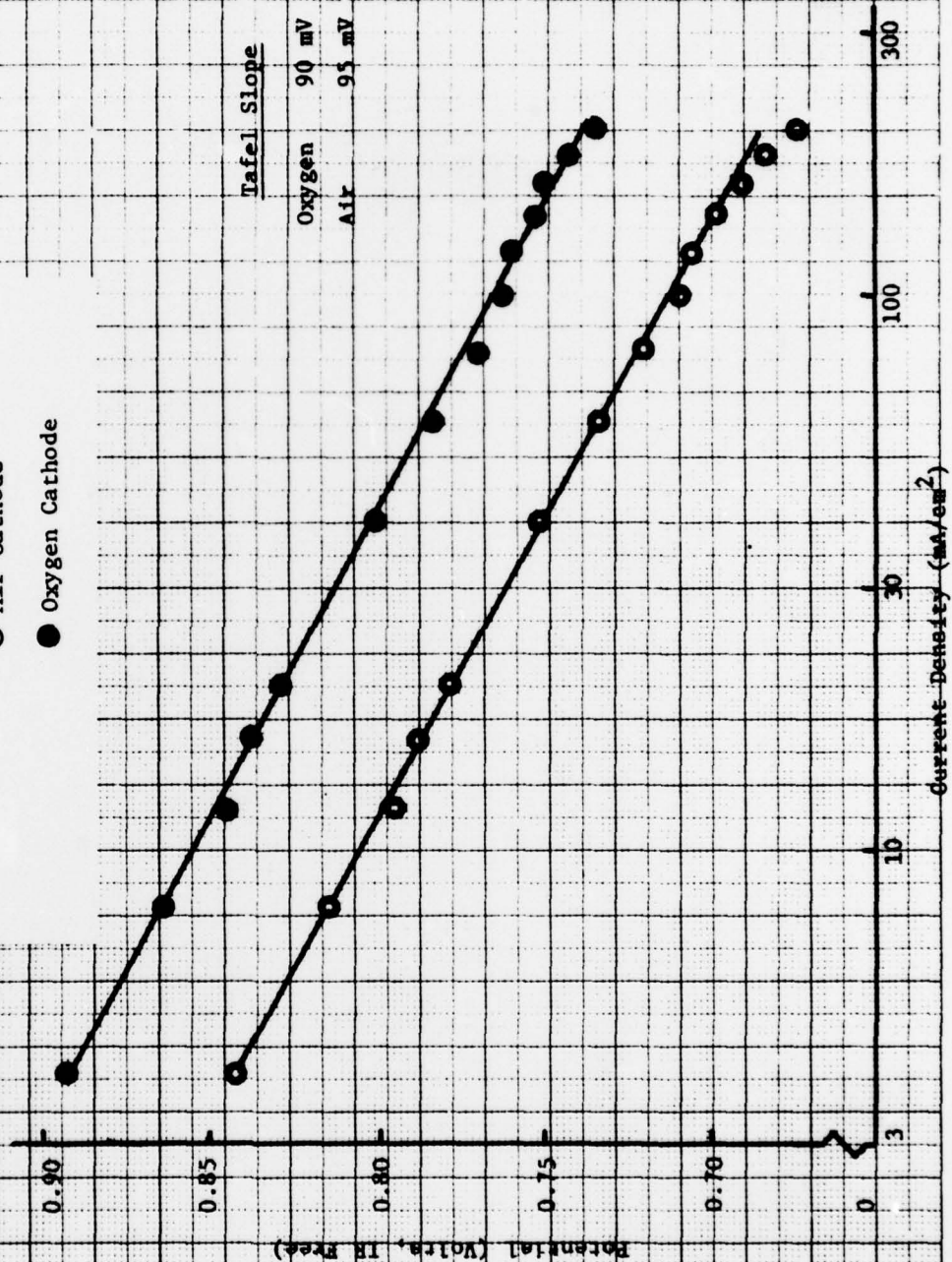


Figure 14
Polarization Curve for Cell ERC-180₂ at 180°C.
Platinum Loading ~0.60 mg/cm².

Terminal Voltage

○ Air Cathode

● Oxygen Cathode



O₂ versus H₂, assembled with 3648-94A Kocite electrodes, are shown in Figure 11. The performance of this cell as a function of time is shown in Figure 12. This cell was normally operated at 200 mA/cm² and has run with very good stability over the test period. Polarization curves for cell ERC-180 are shown in Figure 13. This cell also used Kocite electrodes from electrocatalyst batch 3648-94A. The data plotted in Figure 13 are replotted in Figure 14 to determine the Tafel slope of the cell. As indicated in this figure the cell Tafel slopes on air and oxygen are 95 and 90 mV respectively.

5.3 Summary of Results

The most important results obtained during this contract period are summarized below:

(A) Production of Leached Kocite Materials

The size of leached Kocite material batches was scaled up to 100 to 150 g as part of a general process scale-up to allow the production of 100 to 150 g Kocite electrocatalyst batches. The leaching temperature of Hydral based Kocite materials was raised to and standardized at 180°C. For the first time leached Kocite materials were produced from Kaiser based and Alon based Kocite materials. The structure of the various leached materials was examined by both nitrogen desorption pore volume measurements and Transmission Electron Microscopy.

(B) Kocite Electrocatalyst Production

i. Impregnation of Leached Kocite Materials

Kocite electrocatalysts were produced using both the chloroplatinic acid and platinum diaminedinitrite techniques. Somewhat better platinum dispersions were obtained on a H₂ reduced PDD impregnated electrocatalyst than on the best 15 wt-% CPA impregnated electrocatalyst. However, the latter technique remains the method by which standard electrocatalyst batches will be produced pending fuller testing of PDD impregnated electrocatalysts in fuel cell electrodes.

ii. Kocite Electrocatalyst Structure

Transmission Electron Microscopy was used to examine platinum particle distribution, platinum particle location and electrocatalyst pore structure for several electro-

catalysts. Some large platinum particles and non-uniform platinum particle distributions were observed indicating improved impregnation techniques are desirable. These results also suggest that improved fuel cell performance would result with improved impregnation techniques.

(C) Cell Performance

Kocite electrodes fabricated by both sheet mold and machine rolled methods were used routinely as both cathodes and anodes for the first time. During previous contract periods Pt-black electrodes were used as anodes. In contrast to results obtained previously, 40 wt-% PTFE electrodes appeared to have unstable performance and were subject to flooding. As a result, 45 wt-% PTFE electrodes were used during later cell testing. The most reproducible results were obtained with machine rolled 45 wt-% PTFE electrodes.

Several sets of cells using electrodes from the same electrode batch were assembled under as identical conditions as possible. The performance of these cells was studied to determine the extent of reproducible cathode and anode performance currently attainable with ERC fabricated Kocite electrodes in ERC test hardware. The largest and most reliable set of cells assembled consisted of 15 cells of which 12 cells had a performance level above 550 mV at 200 mA/cm² at 180°C. The average performance of these cells was 575 mV and the best cell was stable at 600 mV at the same test conditions. While better reproducibility is desired, cell performance is clearly improved over that of the previous contract period. X-ray fluorescence measurements show that the variation in cell performance is not a result of variations in electrode platinum loading. The authors believe that the reproducibility problem results primarily from cell to cell variations in assembly technique and incomplete optimization of Kocite electrode structure.

VI. CONCLUSIONS

Based on the results obtained in the last six months in the areas of Kocite particle substrate leaching, Kocite electrocatalyst preparation, and Kocite electrode performance, the following conclusions concerning low cost fuel cell electrodes fabricated from Kocite electrocatalysts are warranted.

- (A) Leaching Hydral based Kocite materials at 180°C rather than 140°C does not alter platinum particle size of the electrocatalyst and gives a support structure which is essentially a replica of Hydral 705 alumina.

- (B) Kocite electrocatalysts for fuel cell applications can be prepared by either chloroplatinic acid or platinum diaminedinitrite impregnation. Actual electrode performance of these electrocatalysts is similar, but appears to favor the latter technique.
- (C) Kocite electrodes can be used as both cathodes and anodes. However, it has not been established that the electrodes used for cathode operation have the structure required for long term reproducible anode performance.
- (D) Alon based Kocite materials can be successfully leached and fabricated into Kocite electrocatalysts. Initial results are promising and starting Kocite materials with a lower carbon content should give higher surface area supports and improved platinum dispersion.
- (E) The reproducibility of cell performance from cell-to-cell has been substantially improved over that of the previous contract period, however, further improvement is clearly desirable.
- (F) More stable and reproducible performance is currently obtained with machine rolled rather than sheet mold Kocite electrodes. Although peak cell performance may be better with sheet mold electrodes, further optimization of sheet mold Kocite electrode structures and fabrication methods will be required to attain desired cell performance reliability with sheet mold Kocite electrodes.

VII. RECOMMENDATIONS

To further improve the performance of Kocite electrocatalysts and Kocite electrodes, and continue their development in H_3PO_4 electrolyte fuel cells, the following recommendations are made.

- (A) Further efforts should be made to achieve improved platinum dispersions using the platinum diaminedinitrite impregnation technique.
- (B) Kocite electrocatalysts made from Alon based Kocite material should be prepared and evaluated in Kocite electrodes.

- (C) The structural analysis of Kocite electrocatalysts should be continued to determine the effect of process conditions and impregnation technique on support properties, platinum particle placement and platinum particle distribution.
- (D) Both sheet mold and machine rolled Kocite electrode structures should continue to be optimized. At this time, which electrode fabrication technique can give the optimal electrode structure for Kocite electrocatalysts has not been established.
- (E) Testing of substantial numbers of cells with both Kocite anodes and cathodes should continue to further examine the reproducibility of cell performance.

VIII. REFERENCES

1. L. B. Welsh, R. W. Leyerle, G. L. Hervert and K. J. Youtsey, "Carbonaceous Catalysts for H_3PO_4 Fuel Cells", MERDC Contract DAAK02-75-C-0011, Final Technical Report, September, 1975.
2. L. B. Welsh, R. W. Leyerle, "Optimization of Pt-Doped Kocite^R Electrodes in H_3PO_4 Fuel Cells", MERADCOM Contract DAAG53-76-C-0014, Interim Technical Report, January, 1977.
3. L. B. Welsh, R. W. Leyerle, "Optimization of Pt-Doped Kocite^R Electrodes in H_3PO_4 Fuel Cells", MERADCOM Contract DAAG53-76-C-0014, Interim Technical Report, January, 1978.
4. TEM results obtained with the cooperation of Professor A. V. Crewe and Mitsuo Ohtsuki at the University of Chicago.

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